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# Curing of a Bisphenol-E Based Cyanate Ester using Magnetic Nanoparticles as an Internal Heat Source through Induction Heating

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ABSTRACT. We report on the control of cyclotrimerization forming a polycyanurate polymer using magnetic iron oxide nanoparticles in an alternating current (AC) field as an internal heat source, starting from a commercially available monomer. Magnetic nanoparticles were dispersed in the monomer and catalytic system using sonication and the mixture was subjected to an alternating magnetic field, causing the magnetic nanoparticles to dissipate the energy of the magnetic field in the form of heat. Internal heating of the particle/monomer/catalyst system was sufficient to start and sustain the polymerization reaction, producing a cyanate ester network with conversion that compared favorably to polymerization through heating in a conventional laboratory oven. The two heating methods gave similar differential scanning calorimetry temperature profiles, conversion rates, and glass transition temperatures when using the same temperature profile. The ability of magnetic nanoparticles in an AC field to drive the curing reaction should allow for other reactions forming high-temperature thermosetting polymers and for innovative ways to process such polymers.

## INTRODUCTION

The art of transforming a monomer into a synthetic polymer has been known for at least 100 years.<sup>1</sup> While the majority of polymerizations developed since that time use thermal heating, other alternatives are available including plasma-induced polymerization,<sup>2</sup> radiation-induced polymerization,<sup>3</sup> microwave induction heating,<sup>4</sup> dielectric heating,<sup>5</sup> and photo-induced thermal front polymerization.<sup>6</sup> Only recently have nanoparticles been embedded in a polymer matrix or coated with polymer for such purposes as drug delivery,<sup>7</sup> antimicrobial applications,<sup>8</sup> selective

ultraviolet protection,<sup>9</sup> increasing polymer performance,<sup>10</sup> as a possible flame retardant,<sup>11</sup> and many others.<sup>12-13</sup>

Mixtures of magnetic nanoparticles and polymers are now being used in combination with induction heating for a variety of purposes. Some examples include using nickel nanoparticles for bonding of composites<sup>14</sup> or induction curing,<sup>15</sup> as well as polymerizations using iron oxide nanochains<sup>16</sup> or titanium nanoparticles.<sup>17</sup> Others have used larger particles in a magnetic field such as using various sizes of nickel to study the heat generated by the particles in a polymer,<sup>18</sup> 1  $\mu\text{m}$  nickel alloy (Nitinol) used to compare polymerizations with conventional or induction heating,<sup>19</sup> or a variety of metal particles from 60 nm to 100  $\mu\text{m}$  used for crack-healing, remolding, or bonding of thermoreversible polymers.<sup>20</sup> Actuation of a reversible gel-to-sol transition using heating from chromium dioxide particles in a nanoparticle-polymer mixture in a magnetic field has been reported.<sup>21</sup> Interestingly, polymerization in a magnetic field without any particles has also been studied.<sup>22</sup>

Primaset® LECy, or 1,1-bis(cyanatophenyl)ethane, is a cyanate ester resin that can be cured at elevated temperatures with a catalyst to form many useful products. As a group, cyanate esters tend to give materials with high glass transition temperatures ( $T_g$ )<sup>23</sup> and very low dielectric constants<sup>24</sup> as well as other useful properties such as low moisture absorption,<sup>25</sup> low volatility,<sup>23</sup> reduced toxicity,<sup>26</sup> resistance to fire,<sup>27</sup> and many others.<sup>28</sup> These properties make cyanate ester resins useful for a wide variety of fields such as applications in aerospace,<sup>29-30</sup> pressure sensitive adhesives,<sup>31</sup> magnet insulation,<sup>32</sup> electric insulators<sup>33</sup> as well as flexible circuitry, surface finishes, photonics, and biomedical applications.<sup>28</sup> Kessler *et al.* have studied the properties of bisphenol-E cyanate ester nanocomposites with embedded nanoparticles of alumina,<sup>34-36</sup> silica,<sup>37-38</sup> zirconium tungstate,<sup>39-40</sup> and recently micro particles of iron oxide coated with silica<sup>41</sup> using

standard polymerization techniques. An earlier study reported on the effects of layered silicates in LECy based nanocomposites.<sup>42</sup> Similarly, the Gu group has investigated the properties of another cyanate ester resin mixed with carbon nanotubes,<sup>43</sup> aluminum nitride-carbon nanotubes,<sup>44</sup> zirconia fibers,<sup>45</sup> silica,<sup>46</sup> and organic rectorite, a layered silicate material.<sup>47</sup> There also exist reports on the properties of cyanate esters with layered silicate<sup>48</sup> or organoclay.<sup>49</sup> To our knowledge, there are no previous reports of the polymerization of the LECy cyanate ester with nanoparticles used as the heat source.

Induction heating, heating of electrically conductive materials by electromagnet induction, historically was used for metal work,<sup>50</sup> but recently has found many uses with magnetic nanoparticles.<sup>15, 51-53</sup> Induction heating offers many advantages over traditional thermal heating such as: the ability to heat only localized areas, the ability to reach high temperatures quickly, its high thermal efficiency, the ability to heat materials internally, and the fact that no contact is required with the material being heated.<sup>18, 54</sup> One example where induction heating would have significant advantages, because of the ability to more readily control the temperature and the uniformity of the heating, would be in the development of ultrahigh molecular weight polyethylene where formation temperatures are low to avoid melting and have been shown to affect the properties of the polymer.<sup>55-57</sup> Use of ferromagnetic and superparamagnetic particles as a localized heat source through the application of an alternating magnetic field can be found in a variety of examples,<sup>14-20</sup> but no instances are found using nanoparticles to drive the curing reaction of high-temperature thermosetting polymers. Here, we report the first polymerization of a high-temperature network polymer driven by the inductive heating of iron oxide nanoparticles dispersed within an uncured resin.

In general, polymerizations of cyanate esters are accomplished through thermal curing of the monomer with an initiator<sup>58</sup> or through photochemically initiated curing.<sup>59</sup> The thermal heating of the monomer is usually done with a slow heating ramp (2-5 K/min) to relatively high temperatures (150-300°C) over a period of a few hours. The photochemical initiation can be done at room temperature, but the sample must be very thin and in most cases the reaction is highly oxygen sensitive. Our use of magnetic nanoparticles in an AC magnetic field as a heat source for the polymerization avoids some of these difficulties.

## EXPERIMENTAL SECTION

Iron (III) chloride hexahydrate (ACS reagent, 97%), iron (II) chloride tetrahydrate (ReagentPlus®, 98%), tetramethylammonium hydroxide solution (25 wt. % in water), and oleic acid (technical grade, 90%) were purchased from Sigma-Aldrich and used without further purification. Likewise, ammonium hydroxide (Certified ACS Plus, 28-30 w/w %) and ethanol (anhydrous, histological) were purchased from Fisher Scientific and used without further purification. Primaset® LECy (1,1-Bis(4-cyanatophenyl)ethane) and a premade mixture of copper (II) acetylacetonate/nonylphenol (1:30 ratio) were provided by the Air Force Research Laboratory, Edwards Air Force Base and used without further purification.

*Preparation of Iron Oxide Magnetic Nanoparticles.*<sup>51</sup> Iron (III) chloride hexahydrate (11.75 g, 43.5 mmol) and iron (II) chloride tetrahydrate (4.3 g, 21.6 mmol) were each separately dissolved in 100 ml deionized, degassed water (bubbling nitrogen, 30 min), sonicated (30 min), and degassed with bubbling nitrogen (5 min). The two solutions were mixed in a 500 ml cylindrical reaction vessel with flat flange using a mechanical stirrer (100 rpm) and nitrogen was bubbled through the combined solution as it was heated to 70°C. Once the solution reached 70°C, ammonium hydroxide (30 ml) was added and the temperature was increased to 80°C. The

solution was held at 80°C for 1 hour and deionized, degassed water and ammonium hydroxide were added as needed to compensate for evaporation and to maintain the reaction solution at pH 8. After 1 hour, the heat was removed and the solution was allowed to reach room temperature. Aliquots (20 ml) were placed in 50 ml centrifuge tubes, centrifuged (1500 rpm, 312xg) for 10 min, and magnetically decanted for the black particles.

To peptize the particles, tetramethylammonium hydroxide (10 ml) was added to each centrifuge tube, the particles were suspended using a vortex, precipitated by centrifugation (10 min, 1500 rpm), and magnetically decanted. An additional portion of tetramethylammonium hydroxide (10 ml) was added to each tube and the particles were suspended, precipitated, and collected. The black, tacky particles were transferred to a beaker, placed into an oven (60°C), and dried overnight.

*Coating of Iron Oxide Magnetic Nanoparticles.*<sup>55</sup> A solution of the dried iron oxide peptized nanoparticles (7 g) and deionized water (280 ml), in a glass beaker, was placed in a sonicating water bath (20 min, Fisher Scientific Mechanical Ultrasonic Cleaner FS60) to suspend the particles and then into a high intensity ultrasonic processor (5 min, Sonics Vibra-Cell VCX 750) to break any formed aggregates. Oleic acid (28 ml, 99.1 mmol) was added to the solution which was again placed into the sonicating water bath (10 min). The solution was transferred to a 500 ml cylindrical reaction vessel with flat flange and heated (80°C) with mechanical stirring (100 rpm). After 1 hour, the heat was removed and the solution was allowed to reach room temperature. Aliquots (10 ml) of the colloid solution were placed in 50 ml centrifuge tubes and ethanol (35 ml) was added to each tube. The tubes were centrifuged (7500 rpm, 7800xg) for 15 min and magnetically decanted for the black particles. The oleic acid coated iron oxide

nanoparticles were removed from the centrifuge tubes and dried in air. The dried nanoparticles were stored in a refrigerator at 4°C.

*Polymerization of Primaset® LECy using Induction Heating.* Oleic acid coated iron oxide nanoparticles (10.5 mg), premixed (1:30 ratio) copper (II) acetylacetonate/nonylphenol catalytic system (41.4 mg), and LECy (1.00 g) were added to a 4 ml glass vial and mixed using a vortex (30 sec). The materials were further mixed using a sonicating water bath (20 min, Branson Ultrasonic Cleaner B200) then degassed by sonication (30 min, Cole-Parmer Ultrasonic Cleaner 8890-DTH – degas setting) and further suspended by the sonicating water bath (5 min). The vial was quickly placed into the induction heater and the temperature measured from above using a thermal camera (FLIR Systems ThermoVision A20). The reaction vial was held in the induction heater coil, as well as insulated, by a handmade Styrofoam piece shaped to fit the coil. The induction heater was controlled using the power setting which corresponds to adjusting the voltage and ramped to 90°C, held at that temperature for 1 hour, then ramped to 120°C or the highest temperature achieved with maximum power and held for an additional hour. After cooling the vial was removed from the induction heater and the formed polymer was characterized.

*Polymerization of Samples in Laboratory Oven.* Premixed (1:30 ratio) copper (II) acetylacetonate/ nonylphenol (0.04 g) and LECy (1.00 g) were added to a vial and mixed by hand for a few minutes to achieve uniformity. The liquid mixture was then de-gassed at 300 mm Hg for 30 minutes at room temperature. The de-gassed mixture was then poured into a silicone mold (RZ2364A/B from Silpak, Inc.) cured overnight at room temperature followed by 1 hour at 160°C and finally placed in a Carbolite convection oven with temperature monitored by an internal thermocouple. To mimic the actual temperature profile from the induction heating

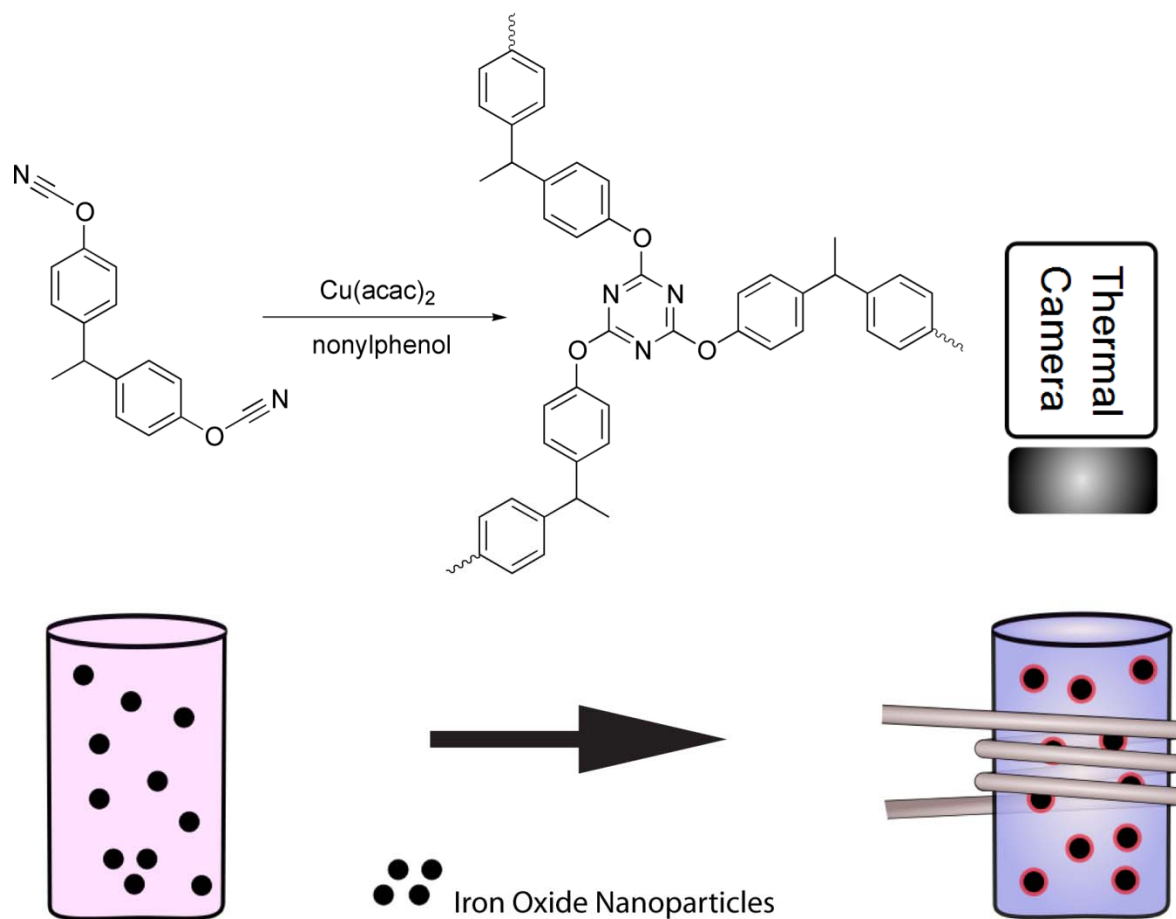


experiments, the oven was ramped at 5°C/min to 90°C then held at 90°C for 1 hour. Following this, the oven was ramped at 5°C/min to 110°C and held at 110°C for 1 minute. The set-point was then reduced to 105°C and held for 1 hour. During this period, the temperature slowly drifted downward, reaching 105°C in a few minutes. This profile mimics the sample temperature seen in Figure 3.

## RESULTS AND DISCUSSION

The general synthetic strategy, as illustrated in Figure 1, is mixing magnetic nanoparticles, the LECy monomer, and an initiator consisting of a mixture of copper (II) acetylacetonate [Cu(acac)<sub>2</sub>] and nonylphenol, then placing the mixture in an alternating magnetic field of selected frequency and amplitude for a given time. The temperature is monitored by a thermal camera placed directly above the sample. This procedure has the advantages of allowing temperatures to be reached quickly, the sample being heated uniformly inside the coil and from within instead of by external heating, allowing for lower temperatures to be used, and the process just lasting two hours. Recent, not yet characterized, reactions suggest a much quicker polymerization time is also possible. Detailed reaction conditions can be found in the Experimental section, but the procedure is summarized here. In a 4 ml glass sample vial was weighted, in order, iron oxide nanoparticles (1% w/w) then 4phr of premixed Cu(acac)<sub>2</sub>/nonylphenol (1:30 ratio) initiator and finally LECy monomer. Cu(acac)<sub>2</sub>/nonylphenol is a widely used catalyst system for cyanate esters<sup>60</sup> in which the nonylphenol provides a proton source to initiate the cyclotrimerization and the copper compound acts as an accelerator. The mixture was sonicated for 20 minutes, degassed by sonication for 30 minutes, and sonicated again for an additional 5 minutes. The vial was quickly placed into the induction heater coil and an appropriate field was applied to hold the temperature at 90°C for about one hour and then

120°C for another hour at which time the vial was cooled to room temperature and the polymer characterized. The field amplitude needed at the various stages of the polymerization depended on the concentration of the particles in the mixture, and their intrinsic heating rate.

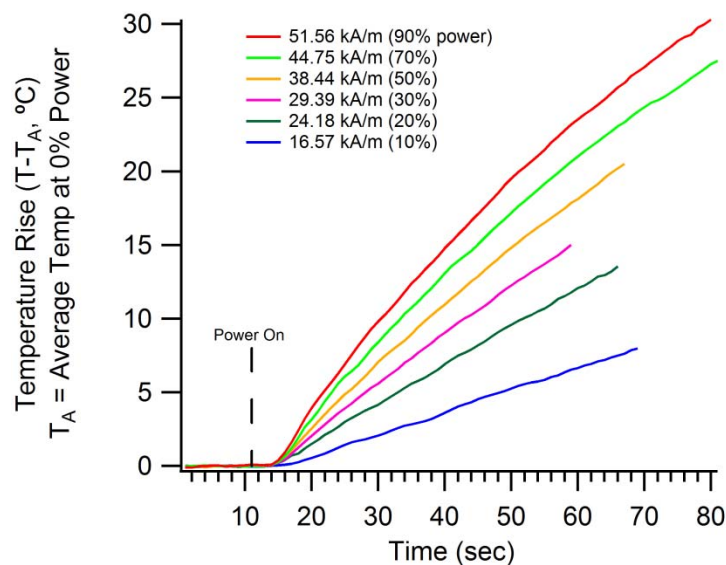


**Figure 1.** Polymerization reaction scheme showing the structure of the Primaset® LECy monomer and formed polymer as well as a graphical representation of the mixture being heated in the coil used for induction heating.

The magnetic nanoparticles used for this polymerization were synthesized by the co-precipitation method<sup>61</sup> due to the relative ease of producing and functionalizing the surface of the particles. While some aggregation is expected from the co-precipitation and coating procedures, the advantages are that it is much simpler than the thermodecomposition heating-up method,

more economical, and the particles generally produce more heat in an induction heater as compared to similarly sized particles from the thermodecomposition method. Iron (II) and iron (III) salts were co-precipitated in ammonium hydroxide under nitrogen then peptized using tetramethylammonium hydroxide. After drying, the particles were coated with oleic acid using an adsorption reaction in water with sonication to form colloidally stable particles. Other ligands were tested, such as 3-aminopropyltriethoxysilane (APS) and 3-(trimethoxysilyl)propyl methacrylate (MPS), but the magnetic nanoparticles coated with oleic acid were the particles that suspended the most readily and stayed suspended the longest in the LECy monomer. The coated particles were characterized by powder X-ray diffraction (XRD), superconducting quantum interference device (SQUID) magnetometry, thermogravimetric analysis (TGA), and dynamic light scattering (DLS). The particle size was measured and gave a magnetic core of 9nm (SQUID), a core of 13.7nm (TEM), and a hydrodynamic diameter of 32nm (DLS). Detailed synthesis steps and relevant data for the magnetic nanoparticles can be found above and in the Supporting Information file.

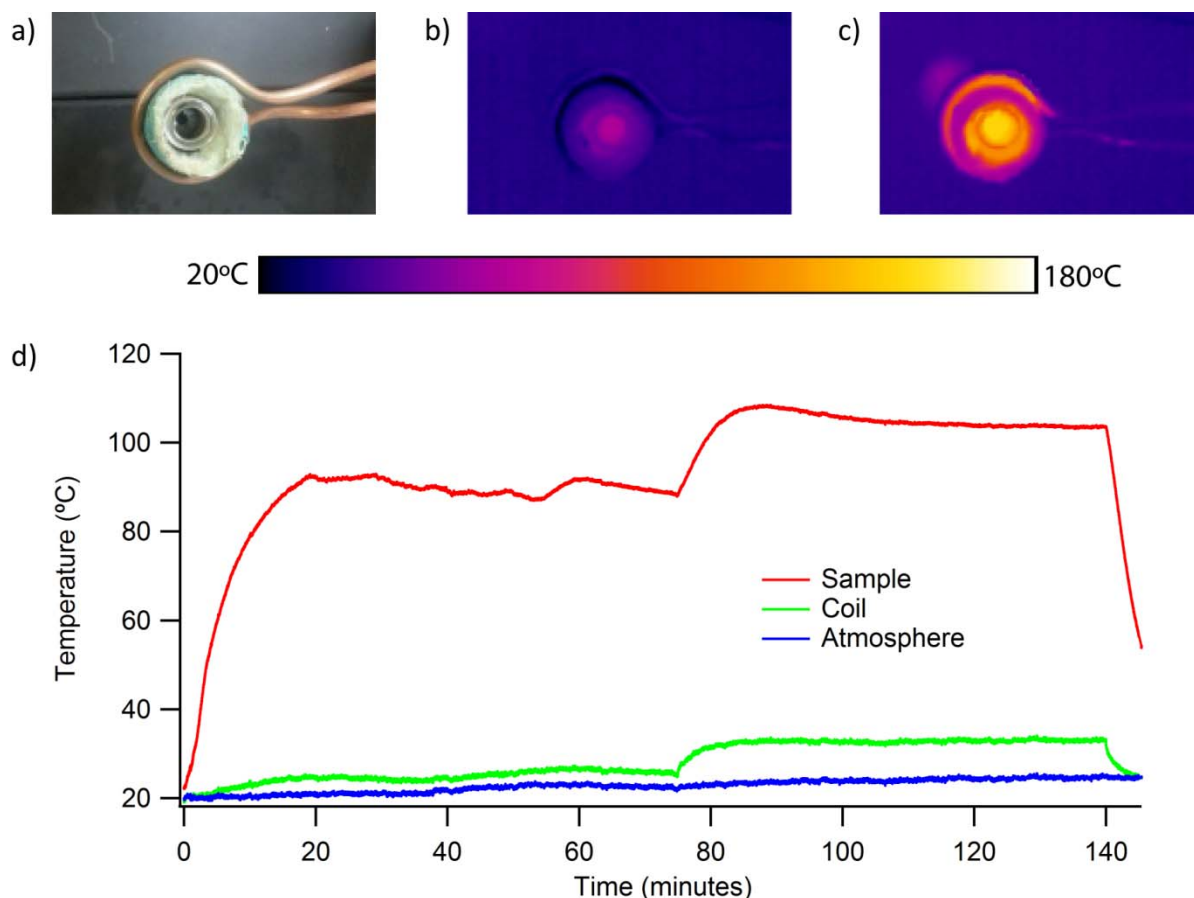
To characterize the energy dissipation rate properties of the magnetic nanoparticles the specific absorption rate (SAR)<sup>62</sup> was determined by suspending the particles in the LECy monomer and placing them in magnetic fields of different amplitudes. In general, the SAR can be understood to mean the heating capacity of a particular material due to induction heating and is measured in watts per gram of material (W/g). Figure 2 shows the observed temperature increase with respect to time for six magnetic field amplitudes for 10.1 mg of magnetic nanoparticles in 1.01 ml of LECy. The general trend is an increase in the rate of heating with increasing magnetic field strength. SAR values and calculations are available in Supporting Information.



**Figure 2.** Initial rates of temperature rise as a function of field amplitude at selected induction heater power plotted as a change in temperature versus time. All experiments were run at a frequency of 233 kHz. The initial rate increases are used in the SAR calculations (Supporting Information)

The alternating magnetic field used for the polymerization of LECy monomers was generated using a HFI 3 kW RF heating system manufactured by RDO Induction Power Supplies and the temperature at the surface of the polymerization was measured using a FLIR ThermoVision A20 infrared thermal camera. The coil used to create the magnetic field was a 4-turn solenoid coil made from 3.2 mm (1/8") copper tubing with an outer diameter of 34 mm and a height of 30 mm. The surface temperatures of the sample, coil, and the environment were captured and then plotted as a function of time, as shown in Figure 3. The target was to heat the material to 90°C for 1 hour then increase the temperature to 120°C for an additional hour. As seen in Figure 3d, the surface temperature of the polymerization sample was held at 90°C by adjusting the power of the induction heater as needed and then was raised to the maximum power possible in the induction heater. For the experiment shown in Figure 3d, the highest temperature reached was

about 110°C, but other experiments were held at or above 120°C. As would be expected, experiments showed that a higher weight percent of magnetic nanoparticles (2% or 3%) requires much less power to reach the desired temperature and can also reach the temperature sooner. A similarly prepared sample without nanoparticles was tested in the induction heater and no significant rise in temperature was observed and the sample did not polymerize after two hours. Those results and the large difference in sample and coil temperatures seen in Figure 3d, signifying that energy would flow from the sample to the coil and not vice-versa, indicate that the resin is cured through heat generated by the magnetic nanoparticles.



**Figure 3.** View from above the sample in the coil for induction heating as shown (a) as a picture before heating, (b) as a thermal image before applying the AC magnetic field, and (c) as a

thermal image after applying the AC magnetic field. (d) Plot of the temperatures of the sample, induction heating coil, and the atmosphere versus time.

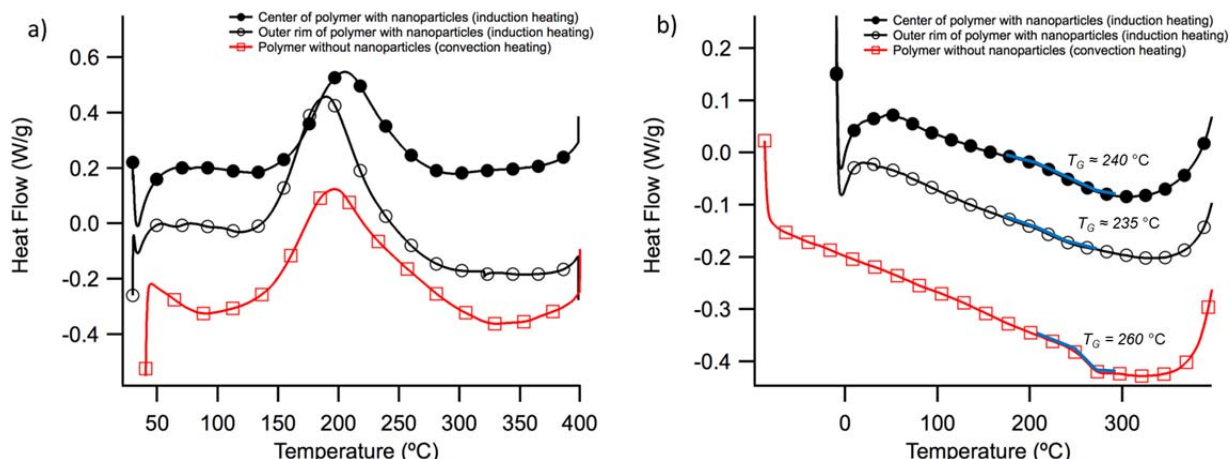
Magnetic nanoparticles respond to alternating magnetic fields to dissipate heat through two mechanisms: Brownian motion and Néel relaxation. The Brownian contribution is due to rotation of the particles in a fluid and depends on the viscosity of the fluid and the hydrodynamic volume of the particle. In contrast, the Néel contribution is due to internal dipole rotation and depends on the magnetocrystalline anisotropy, which depends on the nature of the magnetic material, and the magnetic volume of the particle. It is likely that both Brownian motion and Néel relaxation contribute to the initial heating of the particles, but as the viscosity of the monomer increases the Brownian contribution would decrease. This is suggested by the need to increase the power of the induction heater to maintain a constant temperature as well as the slight decrease in surface temperature during the second hour of heating at maximum induction heater power.

The polymer that formed after induction heating was a glassy solid at room temperature and had an opaque glossy black color due to the embedded nanoparticles. While the bulk polymer was opaque and not much detail could be seen, when the sample was sectioned for characterization by transmission electron microscopy (TEM) the polymer appeared transparent orange and small parallel aggregates could be seen with the naked eye, mainly near the outer edge of the polymer (see Supporting Information). For comparison, a polymer sample produced from the thermal curing of LECy that did not contain nanoparticles was a transparent, light orange color. Once thinly sliced, the polymer produced through induction heating looked no different to the naked eye than the polymer made through convection heating with the obvious addition of nanoparticles.

DSC was used to understand the degree of cure attained by induction heating of the dispersed magnetic nanoparticles. Figure 4 shows DSC thermograms of inductively cured LECy with dispersed magnetic nanoparticles as well as a LECy sample cured traditionally in a normal lab oven with the same temperature history. Two samples were taken from the inductively cured LECy, the first from the outer edge containing some aggregates of the magnetic nanoparticles and the second from the center where the magnetic nanoparticles were well dispersed, as seen by TEM (Figure 5). During the initial temperature scan, each of these samples showed an exothermic peak around 200°C and a similar conversion percentage (Figure 4a). The DSC showed that the samples formed through induction heating had a slightly higher conversion, but the difference between them and the sample formed with convection heating was within the measurement uncertainty. Temperature scans of the inductively cured material taken from the center (homogenous particle dispersion) and edge of the sample (some particle agglomeration) showed integrated residual heats of reaction of around 90 kJ/mol and 70 kJ/mol, respectively. Previous experience has shown that this type of DSC analysis of cyanate ester systems gives an uncertainty of about 10 kJ/mol. A cure scan of LECy monomer containing an identical amount of catalyst and nanoparticles shows an integrated heat of reaction of around 230 kJ/mol, indicating that the induction curing method drove the curing reaction to conversions of 65% - 70% (+/- 5%).

A 65% conversion using induction heating through the use of iron oxide magnetic nanoparticles would likely necessitate a post-cure in industrial applications. However, the conversion is large enough for samples to be de-molded without distortion at room temperature and brought to higher conversion as free-standing parts. Based on a previous study<sup>29</sup> a conversion of 65% is consistent with the times and temperatures utilized. They report that curing

LECy with 2phr of the same catalyst mixture in a laboratory oven for 1 hour at 125°C gives a conversion of 57%, curing for 2 hours at 125°C shows a conversion of 73%, and longer cure times (12 h) gives a 76% conversion rate. This shows our conversion rate to be in good agreement with other cure data for LEcy and suggests that a conversion of 85% or greater, usually desired for optimal performance, could be achieved by further optimizing the process.



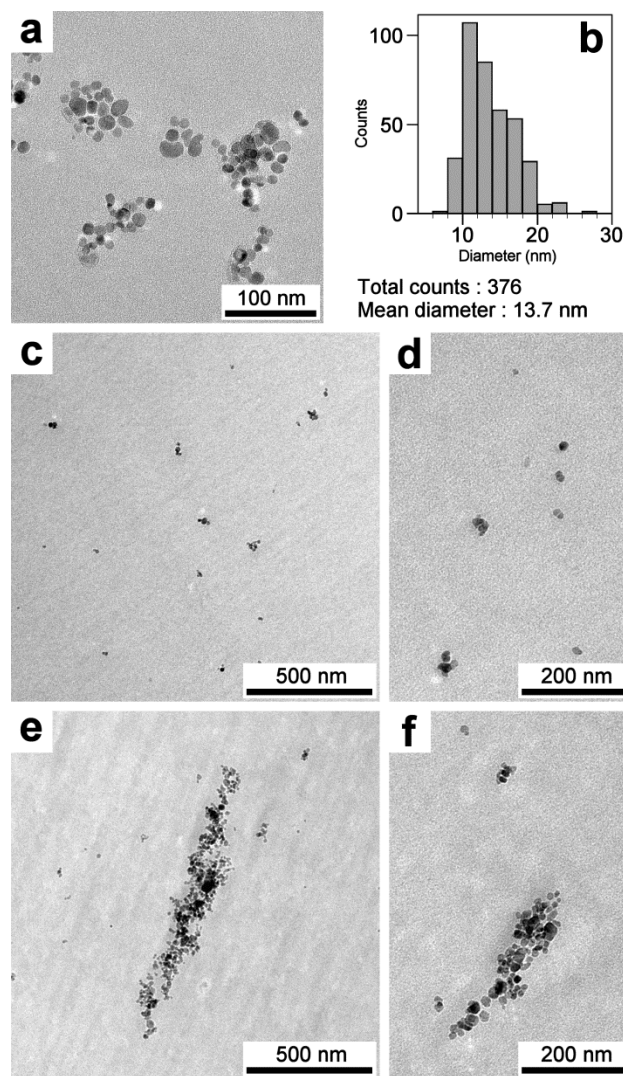
**Figure 4.** DSC thermograms of LEcy samples cured by induction heating with dispersed magnetic nanoparticles (black lines) and cured by traditional convection heating (red line). The initial temperature scans of the “as cured” material (a) show exothermic curves in all three samples representing unreacted monomer with a peak exotherm around 200°C. The second temperature scans of the fully cured (by the initial scan to 400°C) material (b) show a  $T_g$  of around 260°C for the three curves.

Figure 4b shows the second temperature scan in the DSC for the three samples and that the glass transition temperature  $T_g$  of fully cured material (by the initial heating scan to 400°C) is not strongly affected by the presence of the magnetic nanoparticles. All the samples have a  $T_g$  around 260°C, which is within the expected range for fully cured LEcy with 4phr catalyst mixture. After heating to 400°C, the  $T_g$  values for the inductively cured samples are slightly lower than



for the oven cured sample and are less distinct. These differences may be caused by a small amount of retained water that is released upon heating to temperatures above 200°C. At these elevated temperatures, water will react with uncured cyanate ester groups to produce carbamates while also hydrolyzing a small portion of cyanurate linkages. Both reactions involving water will degrade the network structure resulting in a lower and less distinct glass transition temperature. However, this modest difference in  $T_g$  is only seen when the samples are heated to well above their cure temperature whereas there are not significant differences between the three samples in the “as cured” state. This DSC data demonstrates that the samples produced using induction heating have the same physical properties, such as conversion amount, and the same useful cure and solidification effects as oven heating while providing all the previously stated advantages of an induction cure.

The material was also characterized by TEM, after ultrathin sectioning, to determine the dispersion of the nanoparticles in the polymer (Figure 5). The particles were mainly dispersed (Figure 5c, 5d), but small aggregates of a few particles were observed throughout and larger elongated aggregates were observed mainly near the outer edge of the polymer, corresponding to those seen with the naked eye (Figure 5e, 5f). It is not clear whether these aggregates would increase<sup>63</sup> or decrease<sup>64</sup> the magnetic susceptibility and heat output of the particles.



**Figure 5.** Transmission electron micrographs of the nanoparticles used in these polymerizations (a) with the corresponding size distribution graph (b). Ultrathin sections of polymer (c-f): (c) dispersed nanoparticles, sometimes forming small aggregates, (d) higher magnification image showing dispersed nanoparticles, (e) elongated aggregate of nanoparticles, (f) higher magnification image showing on elongated aggregate.

## CONCLUSIONS

In this article, we have presented the synthesis of a polycyanurate polymer from the commercial monomer Primaset® LECy using magnetic iron oxide nanoparticles in an AC field

as an internal heat source. The formed polymer showed both the same conversion and  $T_g$  expected, based on the thermal history, as the polymer formed from convection heating without nanoparticles. These results are a good indication that the nanoparticles are not interfering with the expected cure chemistry and that fabrication of a high  $T_g$ , high thermal stability thermoset using induction heating is possible. The TEM images showed the magnetic nanoparticles mostly well dispersed with sometimes aggregation. Additional characterization, including nanocomposite mechanical strength compared to the thermally synthesized polymer, are needed as well as optimization of reaction conditions. However, the experiments reported here indicate that this approach could be a promising alternative for thermal curing of cyanate ester resins such as Primaset® LECy.

## ASSOCIATED CONTENT

### Supporting Information

Characterization details of the magnetic nanoparticles including instrumentation used and results obtained as well as all calculated SAR values and additional TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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